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LASER EXCITATION OF FLUORESCENCE
IN THE A-X SYSTEM OF NH

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I. INTRODUCTION

In the technique of laser-excited fluorescence (LEF), a laser is tuned such that its wavelength matches that of an absorption line of some molecule of interest. Absorption of the laser light results in the production of a fluorescent photon which is then detected. Tuning of the laser across a series of absorption lines of the molecule, a so-called "excitation scan", provides what is in essence an absorption spectrum. The advantages over conventional absorption spectroscopy are several. First, because one measures a positive fluorescence signal on a null background, in contrast to the removal of photons from a continuum, LEF is of considerably higher sensitivity. Concentrations of molecules at ppb levels can easily be detected. Second, laser linewidths of $0.1\text{--}0.3\text{ cm}^{-1}$ can be readily achieved using intracavity etalons; this yields resolution comparable to that of a large spectrometer, providing separation of closely spaced rotational lines and molecular selectivity in cases of overlapping absorption spectra. Third, LEF provides a high degree of spatial resolution through focussing of the beam and of the fluorescence, in contrast to the line-of-sight nature of absorption spectroscopy. Temporal resolution can also be achieved using a pulsed laser; and LEF, like absorption spectroscopy, is non-intrusive, that is, no probe is introduced into the system.

Consequently, LEF holds great promise as a tool for the measurement of species concentrations and internal temperatures in combustion systems. In particular, it is especially well suited as a probe for the transient, radical species which are reactive intermediates and present at low concentration. LEF has been used in flames to detect OH, CH, CN and C_2 , as well as some sulfur-containing molecules.

Prominent among other species for which LEF would be desirable is the NH, or imidogen or imine, radical. It is present in a number of flames involving nitrogen either in air or bound in the fuel, according to detection using conventional absorption and emission spectra¹. It is particularly prominent in flames of ammonia and oxygen² and of hydrocarbons burning in NO_2 ³. NH emission is seen weakly in flames of formaldehyde, methane or methanol and nitric oxide, and is strong in flames of methyl nitrite and ethyl nitrate with oxygen³. An understanding of the

¹A. G. Gaydon, *The Spectroscopy of Flames*, 2nd Ed., Chapman and Hall, London, 1974.

²H. G. Wolfhard and W. G. Parker, "A New Technique for the Spectroscopic Examination of Flames at Normal Pressures", *Proc. Phys. Soc.* **A62**, 722-730 (1949); H. G. Wolfhard and W. G. Parker, "A Spectroscopic Investigation into the Structure of Diffusion Flames", *Proc. Phys. Soc.* **A65**, 2-19 (1952); C. J. Fisher, "A Study of Rich Ammonia/Oxygen/Nitrogen Flames", *Comb. Fl.* **30**, 143-149 (1977)

³A. R. Hall, J. C. McCoubrey and H. G. Wolfhard, "Some Properties of Formaldehyde Flames", *Comb. Fl.* **1**, 53-59 (1957).

chemistry of nitramine propellants may thus well benefit from a technique capable of measuring NH at low concentrations. In addition, LEF can be of use for monitoring reactant or product concentrations for transients in flow systems, in order to measure reaction rates on a bulk⁴ or state-specific⁵ basis. Such rate constants are needed in the establishment of reaction network models of combustion involving NH. Furthermore, these data are of considerable fundamental interest due to the small size of NH, in that it offers the promise of participation in theoretically tractable collisions. The pumping of specific levels of the excited state via LEF would permit the performance of energy transfer studies such as those carried out on the OH radical⁶.

NH has only recently yielded to probing using LEF. In 1977, McDonald, Miller and Baronavski⁷ reported excitation of the $c^1\Pi-a^1\Delta$ transition in the ultraviolet. The metastable a-state NH was produced by photolysis of HN₃ using the 266 nm frequency quadrupled output of a Nd:YAG laser; and the fluorescence-exciting frequency doubled flashlamp pumped laser was synchronized to the Nd:YAG pulse. McDonald and coworkers were unable to find LEF originating from the ground $X^3\Sigma^-$ state in their system. Gelernt and Smith⁸ formed ND from a pulsed discharge in mixtures of ND₃ in argon. They excited the $b^1\Sigma^+$ metastable into the $c^1\Pi$ state using visible laser light, and detected the resulting ultraviolet fluorescence in the $c\rightarrow a$ transition. The use of a short pulsed laser (N₂-laser-pumped dye) permitted the measurement of radiative lifetimes in $c^1\Pi$.

The electronic states of NH involved are shown in Figure 1. The $A^3\Pi_1-X^3\Sigma^-$ transition should be an ideal candidate for LEF, on the basis of previous absorption and emission studies. Excitation of LEF in the

⁴I. Hansen, K. Höinghaus, C. Zetsch and F. Stuhl, "Detection of NH ($X^3\Sigma^-$) by Resonance Fluorescence in the Pulsed Vacuum uv Photolysis of NH₃ and its Application to Reactions of NH Radicals", *Chem. Phys. Letters* **42**, 370-372 (1976); C. Zetsch and I. Hansen, "Rate Constant for the Reaction of NH ($X^3\Sigma^-$) Determined by Pulsed Vacuum uv Photolysis of NH₃ and Resonance Fluorescence Detection of NH", *Ber. Bunsen. Phys. Chem.* **82**, 830-833 (1978).

⁵J. L. Kinsey, "Laser-Induced Fluorescence", *Ann. Rev. Phys. Chem.* **28**, 349-372 (1977).

⁶R. K. Lengel and D. R. Crosley, "Energy Transfer in $A^2\Sigma^+$ OH. I. Rotational", *J. Chem. Phys.* **67**, 2085-2101 (1977); R. K. Lengel and D. R. Crosley, "Energy Transfer in $A^2\Sigma^+$ OH. II. Vibrational", *J. Chem. Phys.* **68**, 5309-5324 (1978).

⁷J. R. McDonald, R. G. Miller and A. P. Baronavski, "Photofragment Energy Distribution and Reaction Rates of NH from Photodissociation of HN₃ at 266 nm", *Chem. Phys. Letters* **51**, 57-60 (1977).

⁸B. Gelernt and A. L. Smith, "Tunable Laser Fluorescence Studies of the Metastable $b^1\Sigma^+$ State of the ND Radical", *Chem. Phys. Letters* **60**, 261-264 (1979).

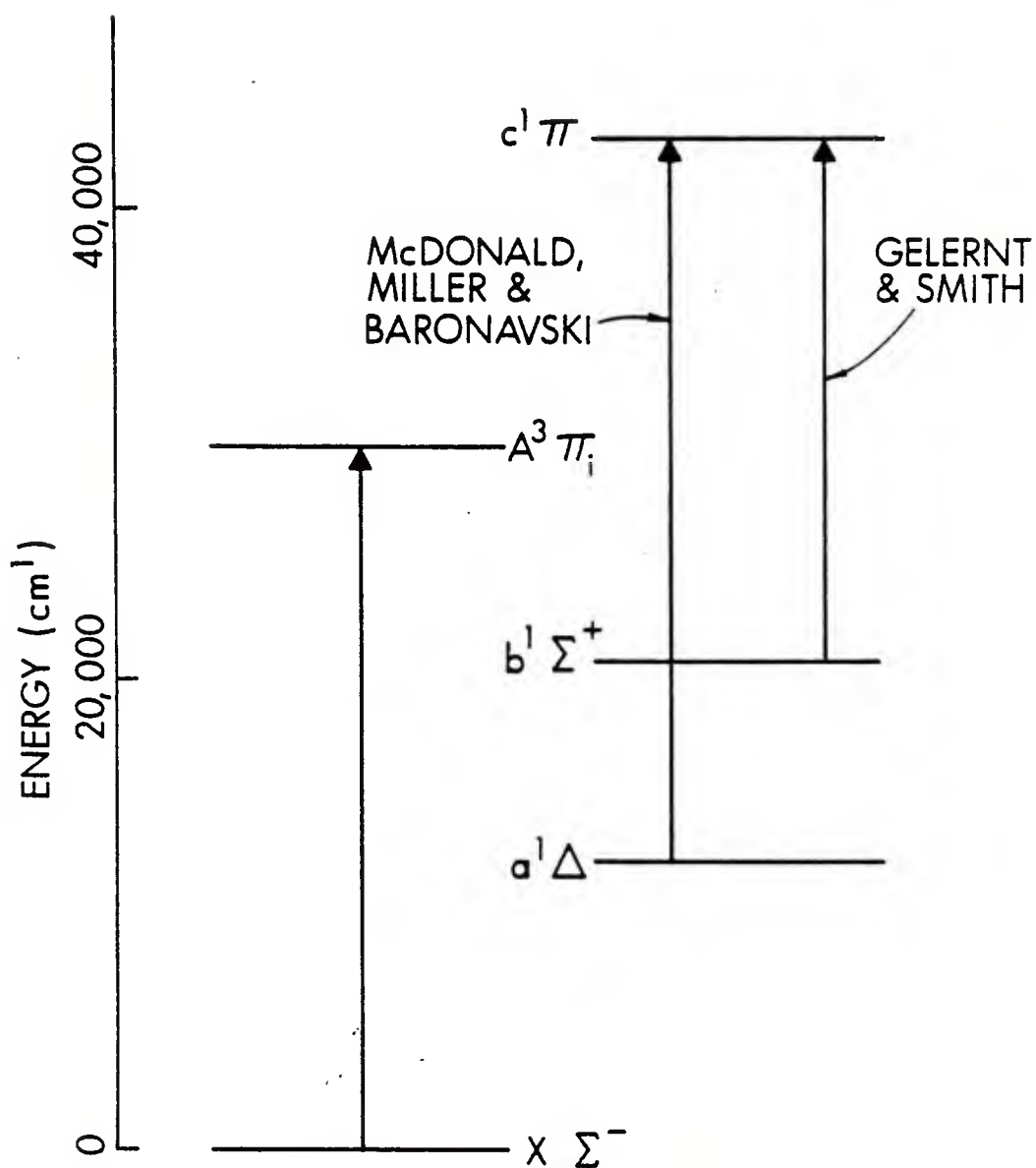


Figure 1. Electronic state diagram for NH. The metastable states excited by previous workers are indicated in addition to the A-X system.

A-X system was first observed in this laboratory⁹ and is the subject of this report. We have since learned that LEF in flames has now also been observed by C. Morely at Shell Thorton Research Center in Chester, England, and by M. Steinberg and K. Schofield at the University of California at Santa Barbara.

LEF in the A-X system probes the ground state of the molecule, which is presumably of the most interest for following its chemical participation. The ability to also excite NH from the two lowest-lying metastables, $a^1\Delta$ and $b^1\Sigma^+$, makes it an attractive molecule for comprehensive inquiry concerning the relative participation of electronically excited states in reaction networks, combustion or otherwise.

II. EXPERIMENTAL DETAILS

The experimental apparatus is illustrated in Figure 2. Ammonia, usually diluted in nitrogen or argon, was rapidly flowed through a stainless steel fluorescence cell with diameter 5 cm; the pressure was typically 18 torr total with 1.5 per cent NH_3 . A 2.45 GHz discharge was applied approximately 10 cm (100 nsec) upstream of the excitation region, using an Evenson cavity surrounding a quartz inlet tube. The pressures used were chosen for maximization of signal levels in our particular system, and were measured using an Alphatron gauge located on a sidearm downstream from the excitation region.

The LEF apparatus was quite standard. The dye laser is a frequency-doubled, flashlamp-pumped type (CMX-4), narrowed to a laser linewidth of $\sim 0.34 \text{ cm}^{-1}$ in the ultraviolet by means of an intracavity etalon. Rhodamine 640 was used for excitation of the (0,0) band near 3360\AA , and rhodamine 6G for the (1,0) band near 3050\AA . Automatic scanning of the main birefringent tuning element, the frequency doubling crystal, and the etalon are accomplished using a scanner accessory.

The unfocussed laser beam was incident upon a plane cell window. After exiting the cell, it was detected by a filtered 1P28 photomultiplier in order to monitor its intensity (in particular, to check that the frequency doubling crystal maintained its proper synchronized alignment during scanning). The fluorescence, viewed at right angles to the exciting beam, was focussed onto the slit of a 0.35 m Heath monochromator operated with a bandpass between 4 and 45\AA , depending on the experiment. The detector was an EMI 9558 QA photomultiplier.

⁹W. R. Anderson and D. R. Crosley, "Laser-Excited Fluorescence in the A-X System of NH", *Chem. Phys. Letters*, in press, 1979; W. R. Anderson, D. R. Crosley, J. E. Jones and J. E. Allen, Jr., "Observation of Laser-Excited Fluorescence in the A-X System of NH", *Eastern Sectional Meeting of the Combustion Institute, Miami Beach, Florida, November 1978*.

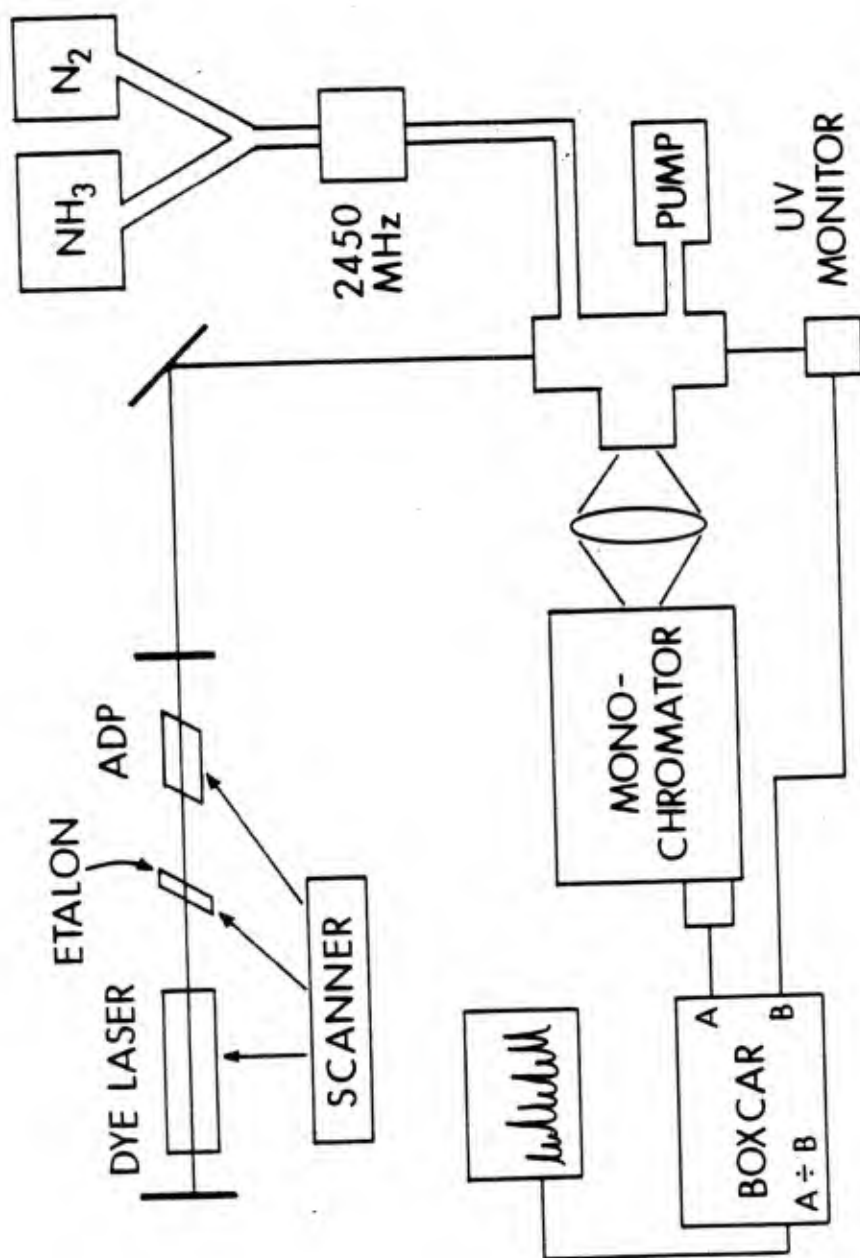


Figure 2. Schematic diagram of the apparatus. Ar was used in place of N_2 in some of the experiments.

After preamplification (and subsequent attenuation, when necessary) the output of each photomultiplier was fed into one side of a dual-channel boxcar integrator (PAR model 162 with 164 plug-ins and digital integration). In some cases, ratioing of the fluorescence and laser intensity signals was done within the boxcar, as indicated in Figure 2, in order to provide a first-order correction for laser intensity drift. In other cases, the direct output of channel A was used. This was then fed to a strip-chart recorder.

Laser repetition rates of 10 Hz were used in conjunction with a typical final time constant of 1 sec. The laser pulse is ~ 1 μ sec long, somewhat greater than the collision-free radiative lifetime of $A^3\Pi_1$ of ~ 450 nsec¹⁰, so that the fluorescence signal time dependence is largely dictated by the temporal shape of the laser pulse. The boxcar was typically operated in a sample-and-hold manner using a gate width of 100 to 200 nsec. The boxcar was triggered by the output of a photodiode viewing the initial rise of the flashlamp output, which was much preferable to the use of the manufacturer-supplied trigger-out pulses from the laser. A considerable component of the noise for the low intensity signals was caused by photomultiplier shot noise, and for high intensity signals by jitter in the laser pulse time vs. the trigger time. Stretching out the photomultiplier pulses via an integrating amplifier, and using a larger gate width on the boxcar would thus presumably improve the signal to noise, but the problems were not severe for the quantitative work reported here and such an arrangement was not seriously explored. For the lower intensity energy transfer signal mentioned briefly below, it is probably a must.

In some of the low intensity runs, where larger slits were used, scattered laser light from the cell windows and walls proved to be a nuisance. This could be greatly improved with the use of some relatively simple baffles. Again, this was not so severe a problem as to demand attention during the present work.

III. RESULTS AND DISCUSSION

The experiments undertaken were of three types. The first are the excitation scans, made by scanning the laser while operating the spectrometer at fixed wavelength. Since fluorescence is observed only when the laser is tuned to an absorption line, this provides in essence an absorption spectrum of the molecule. The others were runs made using the laser at fixed wavelength and scanning the spectrometer used to observe the fluorescence. This mode was used to measure the ratio of Franck-Condon factors for the (0,0) and (0,1) bands of the A-X system, and for some preliminary indications concerning collision-induced energy transfer within the A-state.

¹⁰W. H. Smith, "Lifetimes and Total Transition Probabilities for NH , SiH and SiD ", *J. Chem. Phys.* 51, 520-524 (1969).

A. Excitation Scans

Excitation scans were made for the Q-branch region of the (0,0) and (1,0) bands and for the R-branch region of the (0,0) band.

Different observation regions were used in each case. For excitation of the Q-branch of the (0,0) band, the emission detected was either that in the (0,1) band using a large (45Å) bandpass, or by emission in the region near 3369Å where the $P_{Q12}2$, the P_{12} , the $P_{R13}2$, the P_{23} , and the $P_{Q23}3$ lines all fall quite close together, using a narrower (7Å) bandpass. Due to the small Franck-Condon factor ratio (section IIIB), the narrower bandpass offsets the higher transition probabilities and similar signal-to-noise ratios are obtained with either arrangement.

For excitation in the R-branch region of the (0,0) band, observation was made near the Q-head of the (0,0) band at 3360Å. For the excitation scans of the Q-region of the (1,0) band, observation was made at 3372Å with wide slits (45Å bandpass). Here the detected emission was that of the (1,1) band emitted by the $v'=1$ level directly excited, and that of the (0,0) band emitted by the $v'=0$ level which is presumably populated to some degree by vibrational transfer due to collisions with the N_2 or Ar bath gas.

Using a 21-foot grating spectrograph, Dixon¹¹ carried out measurements of well resolved absorption spectra of the (0,0) and (1,0) bands of the A-X system, following flash photolysis of HNCO. His tables for these bands, and his photographic reproduction of the (0,0) spectrum, have provided an excellent guide for the assignment of our excitation scans. In the few cases in which we observed lines of higher rotational quantum number than those found by Dixon, extrapolation of his sequences have provided unambiguous matches to our line positions.

The $A^3\Pi_1 - X^3\Sigma^-$ system has a total of 27 rotational branches connecting the three triplet levels of the upper state with the three triplet components of the lower, in accord with the rigorous selection rule $\Delta J=0, \pm 1$. Of these 27, the nine main branches having $\Delta N=\Delta J$ are the strongest. We have identified at least one excitation for each of the main branches, and for half the satellite ($\Delta N \neq \Delta J$) transitions. The remaining satellites, save the T_{R31} branch which neither we nor Dixon found, are located in the P-branch region which we have not extensively examined.

Figures 3,4 and 5 show the excitation scans for the (0,0) Q-region,¹ the (0,0) R-region, and the (1,0) Q-region respectively, using ~ 0.34 cm laser linewidth. The assignments of individual lines are included in the figures. The sections marked "reset" are places where the scanning mechanism (though not the recorder) were stopped to automatically reset the

¹¹R. N. Dixon, "The 0-0 and 1-0 Bands of the $A^3\Pi_1-X^3\Sigma^-$ System of NH", *Can. J. Phys.* 37, 1171-1186 (1959).

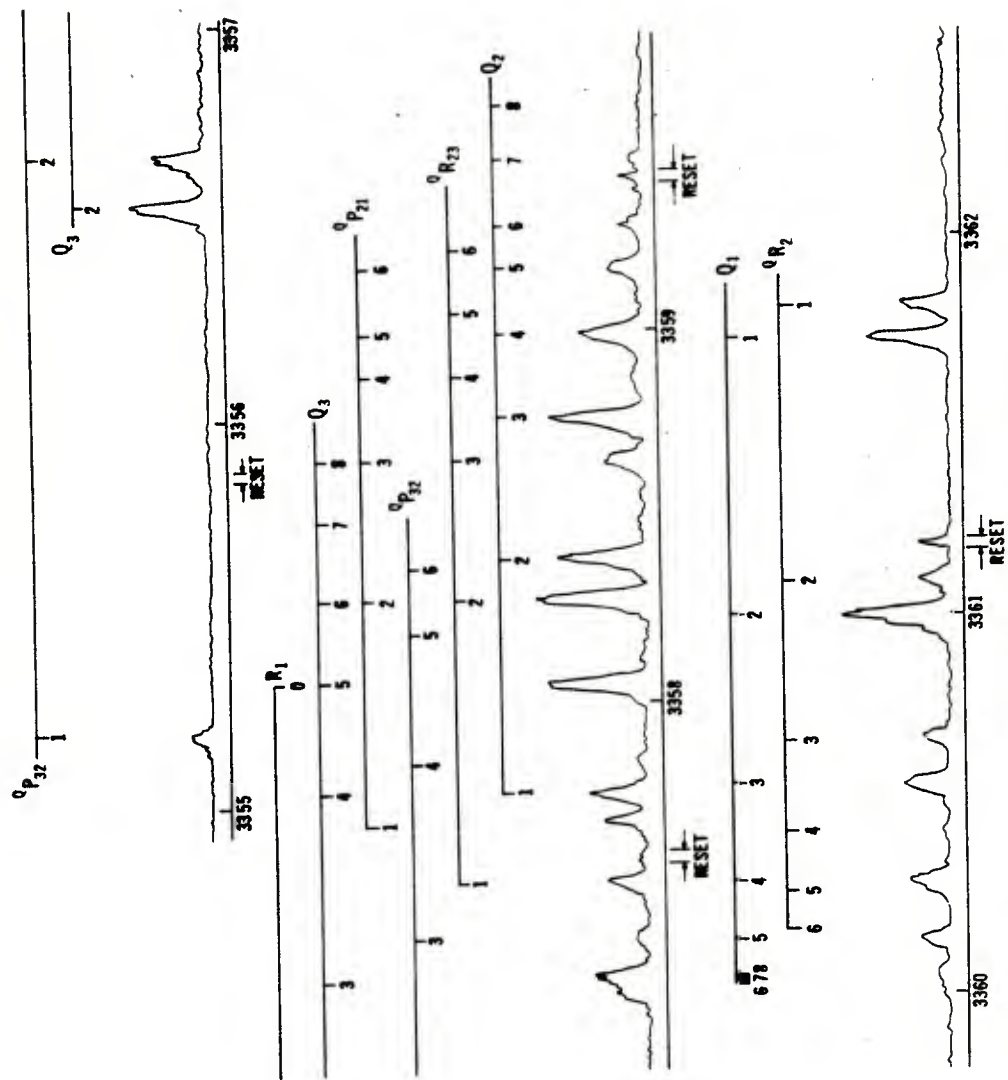


Figure 3. Excitation scan of the Q-region of the (0,0) band. The rotational branches and the ground-state N values are marked. Observation for this particular run was at the dense P-branch blend at 3369Å.

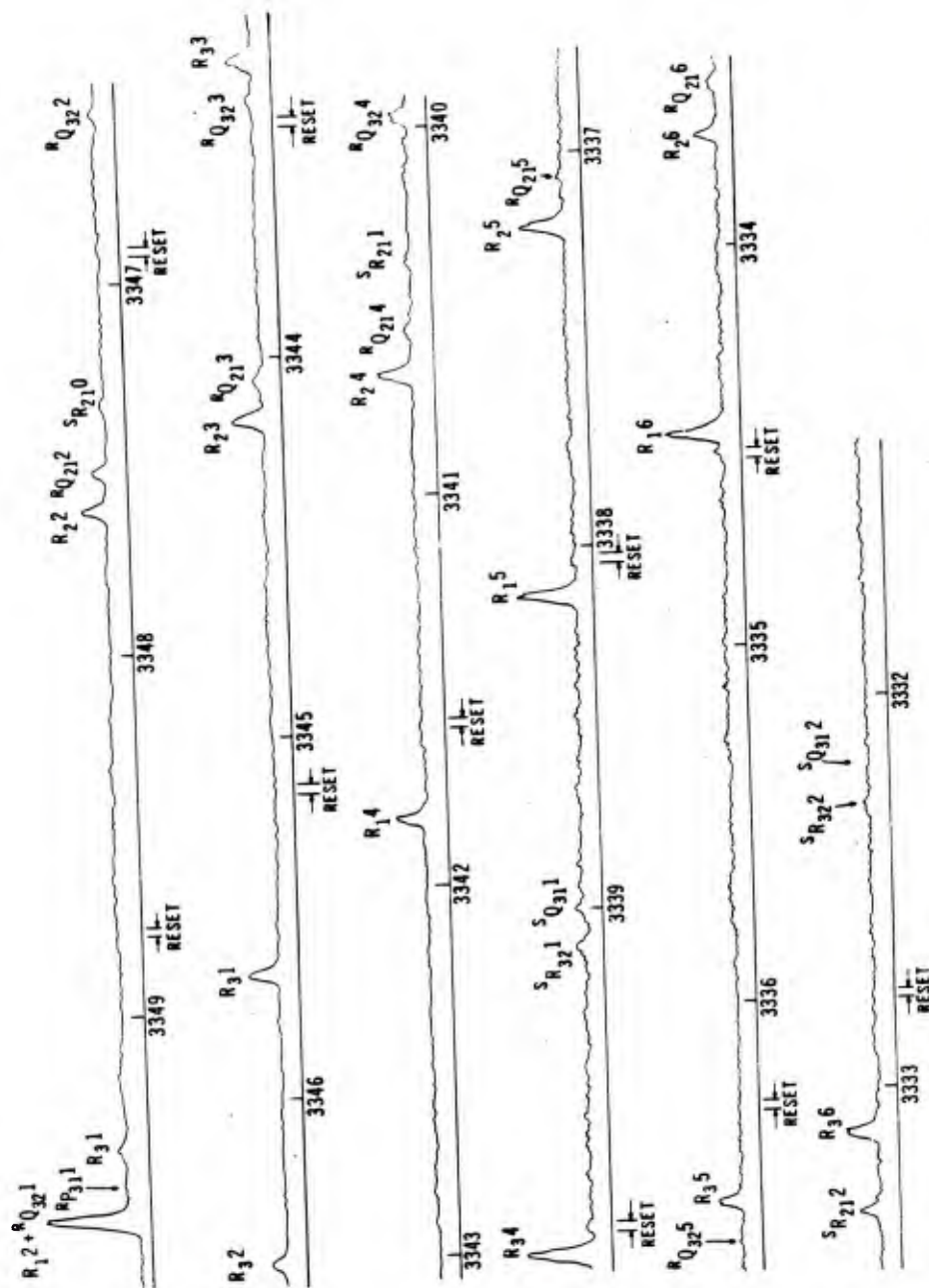


Figure 4. Excitation scan for the R-branch region of the (0,0) band. Fluorescence near the Q-head at 3360 Å was detected.

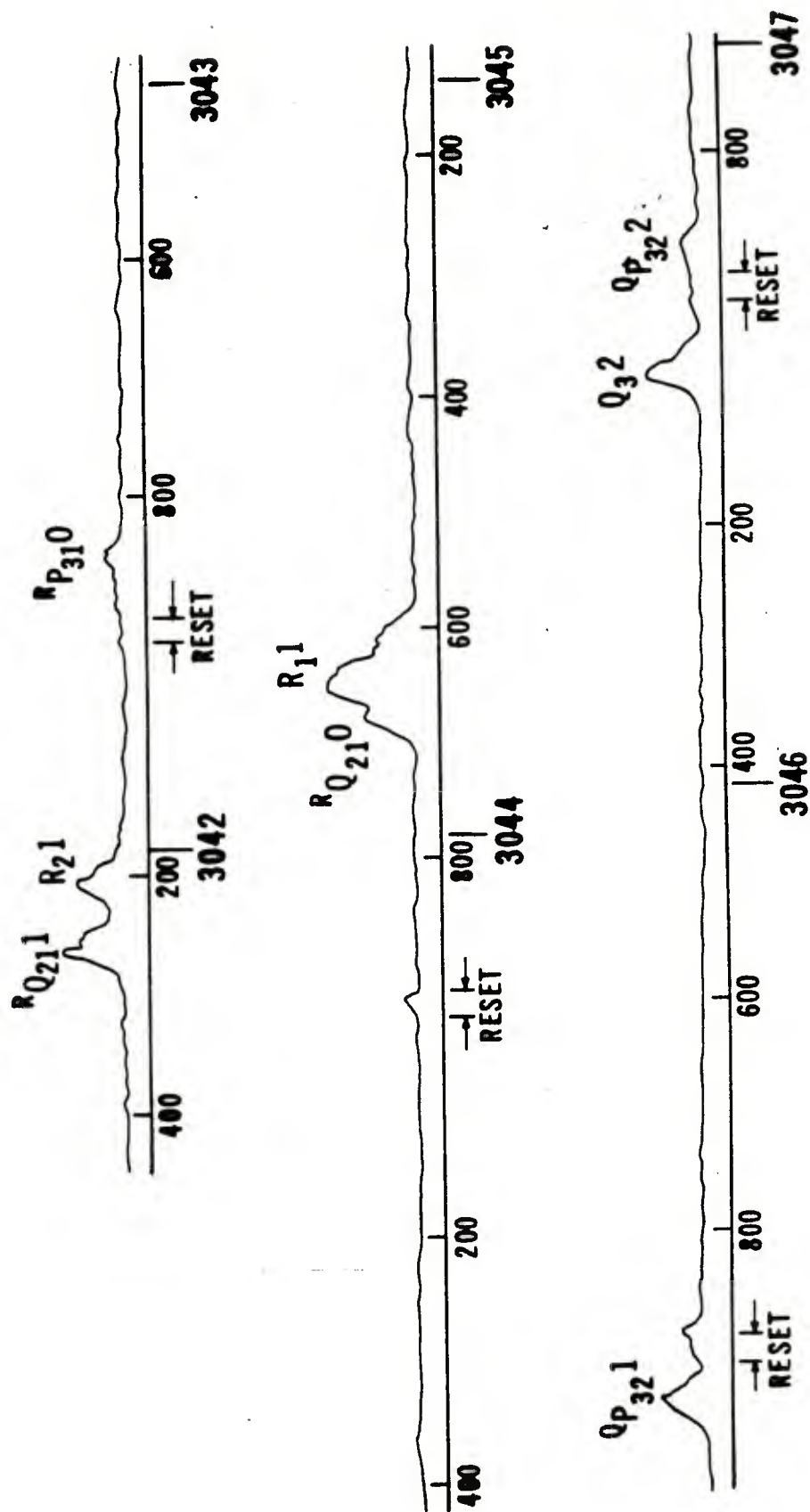


Figure 5. Excitation scan for the Q-region of the (1,0) band. The spectrometer was set at 3372Å, covering the (1,1) Q-head and some of the (0,0) band.

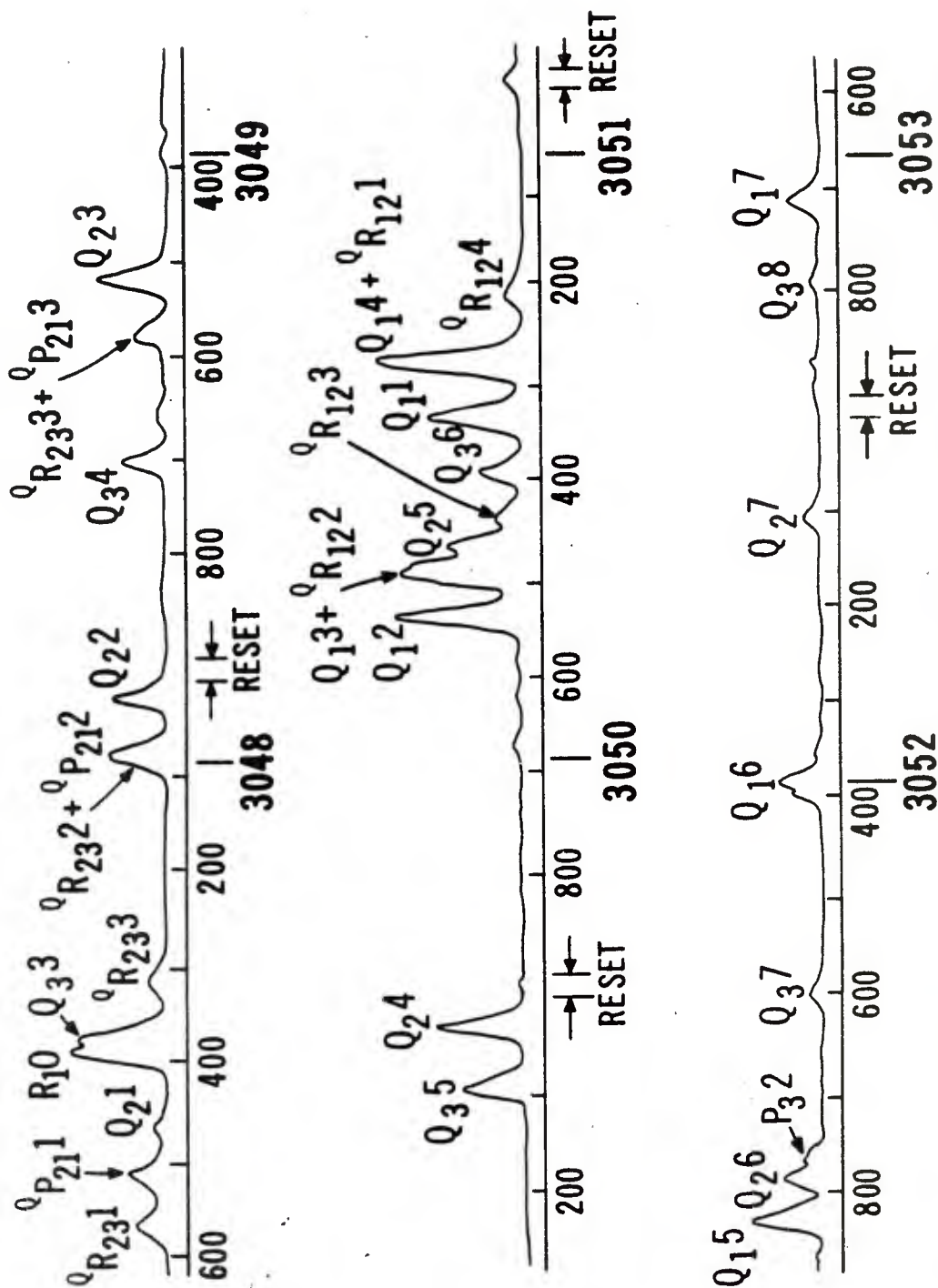


Figure 5. Excitation scan for the Q-region of the (1,0) band. The spectrometer was set at 3372Å, covering the (1,1) Q-head and some of the (0,0) band. (Cont'd)

etalon to the beginning of its free spectral range. While the intensities of nearby lines in a sequence decrease with increasing value of N, they are not quantitatively correct due to drift in the laser intensity throughout each scan. Control of or correction for such drift would permit the intensities of the individual lines to be used to determine populations of each of the ground state rotational levels.

As noted, the assignments were made by comparing the pattern and splittings between adjacent lines with those reported by Dixon¹¹. The results of our measurements of the line positions are given in Tables I, II and III corresponding to Figures 3, 4 and 5, respectively. To obtain these, the splitting between each adjacent pair of lines was measured on the chart recorder and converted to cm^{-1} using the nominal scan speed of both the laser and the chart recorder. The splittings between the corresponding pairs of lines were then computed from Dixon's tables. Since our laser scan is uncalibrated, one does not necessarily expect them to be exactly equivalent. Scaling our laser scan rate by a single factor 1.034 of indicated, for all the splittings observed, provides better agreement with Dixon's values. After making this scaling, our splittings differ from Dixon's in a random pattern. The least squares standard deviation (excluding four splittings with exceptionally large deviations, due to problems in the scan and reset mechanism) of our splittings from Dixon's is $\pm 0.17 \text{ cm}^{-1}$. This is about half the laser linewidth; Dixon estimates his measurements to be good to within $\pm 0.03 \text{ cm}^{-1}$.

Using the measured splittings, and the 1.034 conversion factor, we have computed the wavenumber of each observed line in each sequence by choosing a single normalization line to Dixon. For the Q-region of (0,0), this is Q_32 ; for the Q-branches in (1,1), it is P_32 ; and for the R-region in (0,0) it is R_22 . The frequencies of the lines, determined by us in this way, and as listed by Dixon, are included in the tables along with the splittings.

These excitation maps and corresponding numerical values given in the tables should be of utility in assigning excitation spectra of the A-X system. We have found that, given an approximate location of the laser line ($\pm 1-2A$) using our 0.35 m monochromator, we could pick out the region of excitation after scanning three lines, due to unambiguity in the pattern for a 0.34 cm^{-1} laser bandwidth.

B. The Ratio of Transition Probabilities for (0,0) and (0,1)

The A and X states of NH have very similar potential energy curves, so that those vibrational bands having $\Delta v=0$ dominate the system. This also means that calculated values of Franck-Condon factors $q_{v',v''}$ for $\Delta v \neq 0$ will be very sensitive to details of the wavefunctions used, since the integrals contain large positive and negative contributions which nearly cancel. Two computations of Franck-Condon factors for the A-X

TABLE I. Q-BRANCH EXCITATIONS IN (0,0) BAND

ROTATIONAL BRANCH AND N''	MEASURED ν	$\Delta\nu$	DIXON ν	$\Delta\nu$
Q_3^{2*}	29783.92*		29783.92*	
$Q_{P_{32}}^2$	82.78	1.14	82.82	1.10
Q_3^3	77.27	5.51	77.37	5.45
$Q_{P_{32}}^3$	76.23	1.04	76.44	0.93
$Q_{R_{23}}^1$	74.91	1.32	75.02	1.42
$Q_{P_{21}}^1$	73.66	1.25	74.07	0.95
Q_2^1	73.04	0.62	73.37	0.70
$Q_{P_{32}}^4$	72.32	0.72	72.59	0.78
Q_3^5	70.50	1.82	70.61	1.98
$Q_{P_{32}}^5$	--	\uparrow		\uparrow
		1.98	69.92	2.16
		\downarrow		\downarrow
$Q_3^6 + Q_{P_{21}}^2 + Q_{R_{23}}^2$	68.52	\uparrow	68.45	\uparrow
$Q_{P_{32}}^6$	--	0.95	67.70	1.04
		\downarrow		\downarrow
Q_2^2	67.54		67.41	
		0.87		0.79
Q_3^7	66.67		66.62	
		1.41		1.55
$Q_3^8 + Q_{P_{21}}^3 + Q_{R_{23}}^3$	65.26		65.07	
		0.99		0.92
Q_2^3	64.27		64.15	
		0.92		0.95
$Q_{R_{23}}^4 + Q_{P_{21}}^4$	63.35		63.20	
		1.05		1.08
$Q_2^4 + Q_{P_{21}}^5$	62.30		62.12	
		\uparrow		\uparrow
$Q_{R_{23}}^5$	--	1.52	61.55	1.30
		\downarrow		\downarrow
$Q_2^5 + Q_{P_{21}}^6$	60.78		60.82	
		\uparrow		\uparrow

*The observed frequency was set equal to Dixon's measured value at this point.

TABLE I. Q-BRANCH EXCITATIONS IN (0,0) BAND (Cont'd)

ROTATIONAL BRANCH AND N''	MEASURED		DIXON	
	ν	$\Delta\nu$	ν	$\Delta\nu$
$Q_{R_{23}}^6$	--	1.02 ↓	60.42	1.12 ↓
Q_2^6	59.76	1.24	59.70	1.03
Q_2^7	58.52	1.23	58.67	1.03
Q_2^8	57.29	4.27	57.64	4.90
$Q_1(6-9)$	53.02	0.81	52.74	0.84
Q_1^5	52.18	↑	51.84	↑
$Q_{R_{12}}^6$	--	1.35 ↓	51.47	1.33 ↓
$Q_1^4 + Q_{R_{12}}^5$	50.83	1.13	50.51	1.16
$Q_{R_{12}}^4$	49.70	1.11	49.35	1.12
Q_1^3	48.57	1.03	48.23	1.07
$Q_{R_{12}}^3$	47.54	2.85	47.16	2.67
Q_1^2	44.69	0.85	44.49	0.95
$Q_{R_{12}}^2$	43.84	5.39	43.54	5.45
Q_1^1	38.45	0.81	38.09	0.85
$Q_{R_{21}}^1$	37.64		37.24	

TABLE II. R-BRANCH EXCITATIONS IN (0,0) BAND

ROTATIONAL BRANCH AND N''	MEASURED ν	$\Delta\nu$	DIXON ν	$\Delta\nu$
$R_1 2 + R_{Q32} 1$	29846.63	\uparrow	29846.22	\uparrow
$R_{P31} 1$	--	1.67 \downarrow	47.08	1.80 \downarrow
$R_3 1$	48.30	15.03	48.02	15.31
$R_2 2^*$	63.33*	0.89	63.33*	.97
$R_{Q21} 2$	64.22	1.59	64.30	1.78
$S_{R21} 0$	65.81	6.68	66.08	6.83
$R_{Q32} 2$	72.49	1.34	72.91	1.10
$R_3 2$	73.83	6.97	74.01	7.23
$R_1 3$	80.80	12.74	81.24	12.85
$R_2 3$	93.54	0.96	94.09	1.06
$R_{Q21} 3$	94.50	6.45	95.15	6.74
$R_{Q32} 3$	29900.95	0.91	29901.89	0.95
$R_3 3$	01.86	12.19	02.84	12.32
$R_1 4$	14.05	10.35	15.16	10.17
$R_2 4$	24.40	1.05	25.33	1.11
$R_{Q21} 4$	25.45	\uparrow	26.44	\uparrow
$S_{R21} 1$	--	6.12 \downarrow	28.17	6.42 \downarrow
$R_{Q32} 4$	31.57	0.83	31.86	0.86
$R_3 4$	32.40	7.15	32.71	6.89

* The observed frequency was set equal to Dixon's measured value at this point.

TABLE II. R-BRANCH EXCITATIONS IN (0,0) BAND (Cont'd)

ROTATIONAL BRANCH AND N''	MEASURED ν	$\Delta\nu$	DIXON ν	$\Delta\nu$
$S_{R_{32}^1}$	39.55	0.86	39.60	0.87
$S_{Q_{31}^1}$	40.41	7.46	40.47	7.94
R_1^5	47.87	8.51	48.41	8.26
R_2^5	56.38	↑	56.67	↑
$R_{Q_{21}^5}$	--	5.91	57.84	6.31
$R_{Q_{32}^5}$	--	↓	62.23	↓
R_3^5	62.10	17.83	62.98	18.09
R_1^6	79.93	7.07	81.07	6.83
R_2^6	87.00	1.24	87.90	1.23
$R_{Q_{21}^6}$	88.24	2.07	89.13	2.15
$S_{R_{21}^2}$	90.31	↑	91.28	↑
$R_{Q_{32}^6}$	--	1.90	92.69	2.07
R_3^6	92.21	↓	93.35	↓

TABLE III. Q-BRANCH EXCITATIONS IN (1,0) BAND

ROTATIONAL BRANCH AND N''	MEASURED ν	$\Delta\nu$	DIXON ν	$\Delta\nu$
$P_2 2^*$	32741.64*	1.15	32741.64*	1.14
$^P Q_{23} 2$	42.79	2.97	42.78	3.13
$Q_1 7$	45.76	5.46	45.91	5.76
$Q_2 7$	51.22	4.63	51.67	4.26
$Q_1 6$	55.85	3.77	55.93	3.75
$Q_3 7$	59.62	2.86	59.68	3.15
$P_3 2$	62.48	0.41	62.83	0.34
$Q_2 6$	62.89	0.79	63.17	0.86
$Q_1 5$	63.68	6.20	64.03	6.14
$Q_1 4 + ^R Q_{12} 1$	69.88	0.99	70.17	0.94
$Q_1 1$	70.87	1.01	71.11	0.86
$Q_3 6$	71.88	0.81	71.97	0.82
$Q_{R12} 3$	72.69	0.49	72.79	0.64
$Q_2 5$	73.18	0.51	73.43	0.26
$Q_1 3 + Q_{R12} 2$	73.69	0.75	73.69	0.83
$Q_1 2$	74.44	7.02	74.52	7.52
$Q_2 4$	81.46	1.11	82.04	1.09

*The observed frequency was set equal to Dixon's measured value at this point.

TABLE III. Q-BRANCH EXCITATIONS IN (1,0) BAND (Cont'd)

ROTATIONAL BRANCH AND N''	MEASURED		DIXON	
	ν	$\Delta\nu$	ν	$\Delta\nu$
Q_3^5	82.57	7.24	83.13	6.86
Q_2^3	89.81	3.29	89.99	3.43
Q_3^4	93.10	3.94	93.42	4.19
Q_2^2	94.04	1.03	97.61	1.14
$Q_{R_{23}^2} + Q_{P_{21}^2}$	98.07	4.05	98.75	3.72
$Q_{P_{32}^3}$	32802.12	1.03	32802.47	0.93
Q_3^3	03.15	0.23	03.40	0.21
R_1^0	03.38	2.82	03.61	2.68
Q_2^1	06.20	0.81	06.29	0.74
$Q_{P_{21}^1}$	07.01	0.95	07.03	1.02
$Q_{R_{23}^1}$	07.96	3.96	08.05	5.22
$Q_{P_{32}^2}$	11.92	1.77	13.27	1.04
Q_3^2	13.69	15.06	14.31	15.07
$Q_{P_{32}^1}$	28.75	10.90	29.38	10.45
R_1^1	39.65	0.52	39.83	0.47
$R_{Q_{21}^0}$	40.37	18.61	40.30	19.99

TABLE III. Q-BRANCH EXCITATIONS IN (1,0) BAND (Cont'd)

ROTATIONAL BRANCH AND N''	MEASURED		DIXON	
	ν	$\Delta\nu$	ν	$\Delta\nu$
$R_{P_{31}^0}$	58.98	4.70	60.29	3.73
R_{21}^1	63.68	1.03	64.02	0.88
$R_{Q_{21}^1}$	64.71		64.90	

system have yielded values for q_{01} . Smith and Lizst¹² used RKR curves to obtain $q_{01}=1.98 \times 10^{-4}$, while Hornkohl (quoted by Lents¹³) found a value of 2.97×10^{-5} .

From a diagnostic standpoint, it is desirable to pump at one wavelength with the laser and observe at another, in order to avoid background due to scattered laser light. We have already noted that this formed somewhat of a nuisance in some of our runs. When probing flames, one may have similar difficulties if a combustion chamber is involved. Even when that is not the case, a particle-laden combustion system may present problems due to Mie-scattered radiation at the laser wavelength. Thus it would be desirable to be able to scan the closely-packed Q-region of the (0,0) band -- in order to obtain population distribution and thus temperature information -- while observing in (0,1) to avoid scattered laser light. The calculated values of q_{01} are quite disappointing with regard to such an arrangement, but the difficulties attendant to calculation of these Franck-Condon factors clearly suggested an experimental measurement of q_{01} .

For these runs, the laser was tuned to a specific excitation line of the (0,0) band, assigned by reference to the excitation scans previously carried out. The spectrometer was then scanned across emission in the regions of (0,0) and (0,1) fluorescence. Our initial searches were greatly hampered by looking in the wrong region. According to the wavelengths and spectral constants in several standard compilations¹⁴, we expected the Q-head of the (0,1) band to be located at 3636 Å (we are informed, by private communication from K. Schofield, that the fourth edition of Pearse and Gaydon, which we have not seen, corrects this error). However, as found in more recent work¹⁵, this weak band is actually located with a Q-head at about 3755 Å. Movement of the spectrometer to this region provided instant observation of fluorescence.

The basis of this simple experiment is illustrated in Figure 6. The laser pumps into the level $v'=0$, and the intensities of emission I_{00} and I_{01} in each band are measured. These are related to the Einstein

¹²W. H. Smith and H. S. Lizst, "Franck-Condon Factors and Absolute Oscillator Strengths for NH, SiH, S₂ and SO", *J. Quant. Spect. Rad. Transf.* 11, 45-54 (1971).

¹³J. M. Lents, "An Evaluation of Molecular Constants and Transition Probabilities for the NH Free Radical", *J. Quant. Spect. Rad. Transf.* 13, 297-310 (1973).

¹⁴B. Rosen, *Donnees Spectroscopiques Relatives Aux Molecules Diatomiques*, Pergamon, Oxford, 1970; R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*, 3rd ed., Chapman and Hall, London, 1965; G. Herzberg, *Spectra of Diatomic Molecules*, D. Van Nostrand, Princeton, 1950.

¹⁵J. Malicet, J. Brion and H. Guenebaut, "Contribution a l'etude Spectroscopique de la Transition $A^3\Pi^-_g-X^3\Sigma^-$ du Radical NH", *J. de. Chimie Phys.* 67, 25-30 (1970).

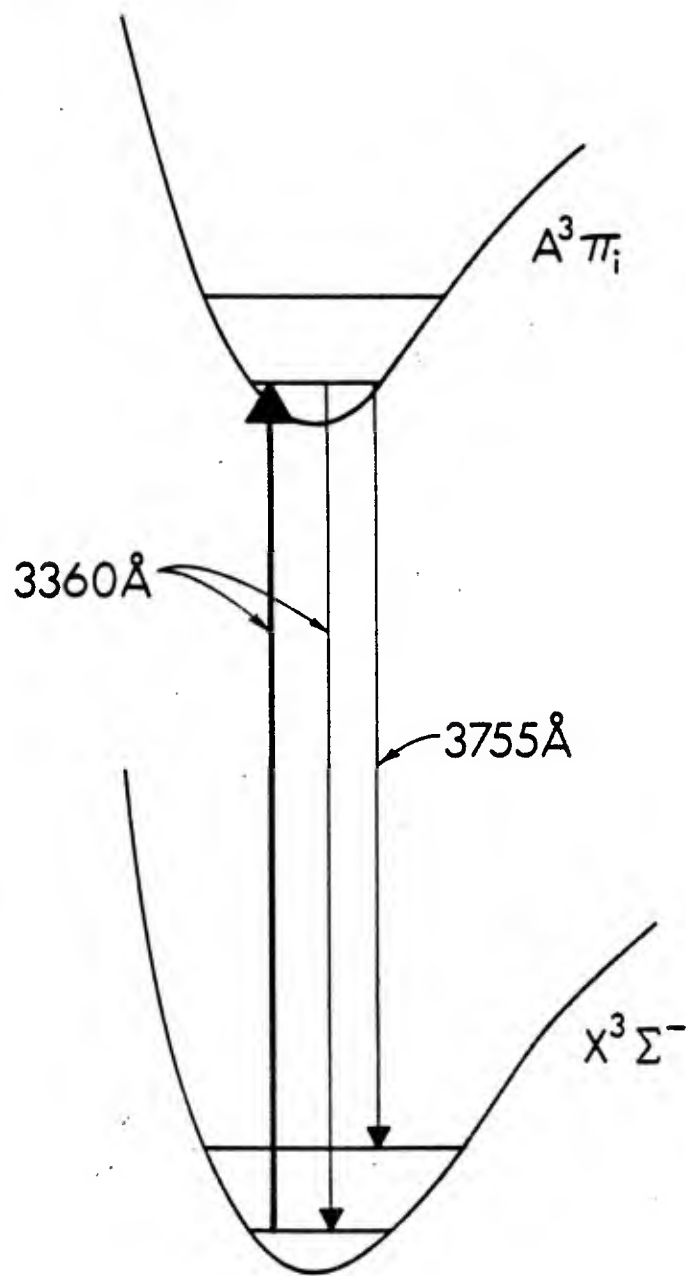


Figure 6. Pumping and fluorescence wavelength, and energy levels, for the determination of q_{01} .

emission coefficients $A_{\nu',\nu''}$ by the separately measured spectrometer response $R(\lambda)$ at each wavelength. The $A_{\nu',\nu''}$ are in turn related directly to the Franck-Condon factors under the assumption of a constant electronic transition moment.

$$\frac{I_{01}}{I_{00}} = \frac{R(\lambda_{01}) A_{01}}{R(\lambda_{00}) A_{00}}, \quad (1)$$

and

$$\frac{A_{01}}{A_{00}} = \frac{\lambda_{00}^3 q_{01}}{\lambda_{01}^3 q_{00}}. \quad (2)$$

But (since q_{02} is very small),

$$q_{00} + q_{01} = 1 \quad (3)$$

permitting the determination of an absolute q_{01} .

Experimental runs were made using both the R_{16} and R_{13} lines as the pump transitions in the (0,0) band. In order to obtain usable signal to noise, it was necessary to use relatively wide slits for the (0,1) band emission. The slits were kept at the same width for the scans of the (0,0) band, in order to avoid problems of correcting for different slit widths. This resulted in considerable laser scatter underlying the actual fluorescent signals, and necessitated a separate measurement of this background. This was done by extinguishing the microwave discharge, so that no NH was produced. Figure 7 shows scans made with the R_{13} pump, of the (0,1) band, the (0,0) band, and the laser scatter in the (0,0) region. These scans were manually integrated using a planimeter in order to obtain the intensity ratio of Eq. 1. These ratios for each run are given in Table IV. The results were then reduced to absolute Franck-Condon factors using Eqs. 2 and 3.

The results yield an Einstein coefficient ratio $A_{01}/A_{00} = 0.0067 \pm 0.0012$; under the assumption of a constant electronic transition moment, this corresponds to a Franck-Condon factor ratio $q_{01}/q_{00} = 0.0093 \pm 0.0017$. This is considerably larger than the values obtained from the theoretical calculations, and is a big enough ratio to establish observation via the (0,1) band as a viable part of a diagnostic technique measuring NH.

TABLE IV. FRANCK-CONDON FACTOR INTENSITY DATA

EXCITATION LINE	RUN	I_{01}/I_{00}
R_1^3	a	0.0158
	b	0.0130
	c	0.0104
R_1^6	a	0.0150
	b	0.0114
Average		0.0131 ± 0.0023

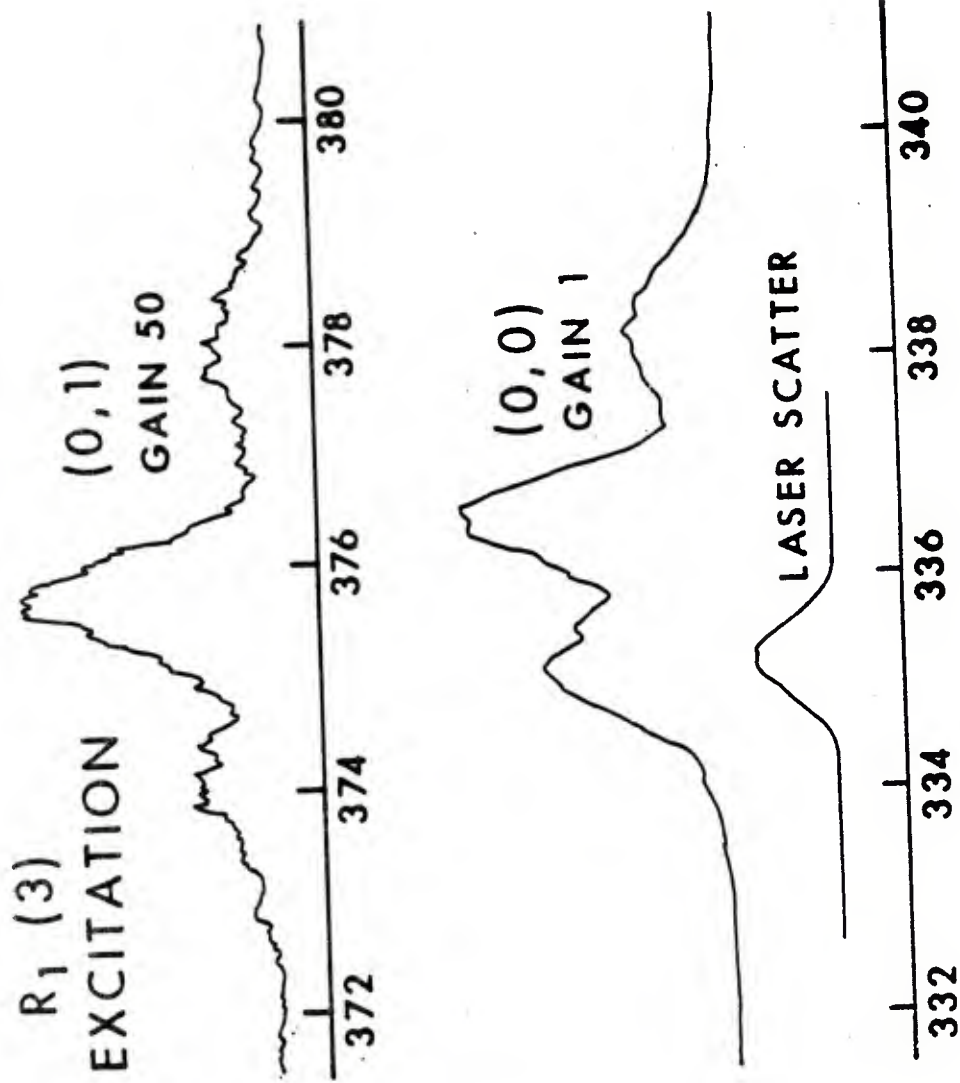


Figure 7. Fluorescence scans upon pumping the R_{13} transition of the $(0,0)$ band. The R-branch emission is at the shortest wavelength, the Q-branches at the center, and P-branches at longer wavelengths. Top: $(0,1)$ band fluorescence. Center: $(0,0)$ band fluorescence plus laser scatter. Bottom: Laser scatter only, obtained with discharge off.

C. Qualitative Energy Transfer Information

At the pressures of the diluent gases involved, typically 20 torr, the A-state NH molecule is likely to suffer rotational energy transfer collisions before radiating. If the rotational transfer cross section is $\sim 50 \text{ \AA}^2$, as in the $A^2\Sigma^+$ state of OH^6 , then at this pressure the collision rate is ~ 100 times the radiative rate. If quenching collisions also occur, the average lifetime is shortened and fewer energy transfer collisions occur before the NH returns to the ground state.

Some preliminary, qualitative information concerning rotational energy transfer was obtained by tuning the laser to a specific line and scanning the monochromator with narrow enough slits ($\sim 4 \text{ \AA}$ bandpass) to achieve some rotational resolution in the spread-out R and P branches. An example is given in Figure 8 where the excitation line is R15, so that the F1(6) level is pumped. This level emits P17, Q16 and a number of weaker satellite intensities. Emission from the initially excited level can be seen by the high intensity in the regions containing these lines. However, some rotational transfer is evidenced by lines for lower lying R and P branches.

For scans having the signal-to-noise ratio of that of Figure 8, one can hardly extract quantitative information concerning the relaxation. However, from an examination of several such scans using different pump lines, we can make some distinction between signal and noise, and reach some conclusions. Unambiguously, rotational energy transfer in NH does occur at ~ 20 torr N_2 . However, the rotational population distribution is far from thermal but remains sharply peaked within the pumped level. More tentatively, the relaxation to nearby levels (small ΔN) appears to occur more rapidly than to levels requiring a larger change in N . There appears to be some propensity for the transfer to occur to other F1 levels in preference to F2 or F3 levels, as is the case in Σ states in OH^6 , NO^{16} and S_2^{17} .

Data on the energy transfer are not only of fundamental interest, but also are important in understanding and modeling the response of the molecule to laser excitation. For a molecule having as coarse a P- and R- branch structure as NH, it may also be of importance in choice of observation wavelength and bandpass, and in design of the data analysis to extract populations from LEF excitation scans. (In fact, the lack of thermalization seen here means different fluorescent wavelengths for each excitation, at least at 20 torr but probably also at 1 atm. This renders even more attractive observation via the (0,1) band.

¹⁶H. P. Broida and T. Carrington, "Rotational, Vibrational and Electronic Energy Transfer in the Fluorescence of Nitric Oxide", *J. Chem. Phys.* 38, 136-147 (1961).

¹⁷T. A. Caughey and D. R. Crosley, "Collision-Induced Transfer Rates Connecting Fine-Structure Levels in S_2 ($B^3\Sigma^-_{u,v'=4}$)", *J. Chem. Phys.*, submitted.

A better design for the flow system and detector electronics, and including baffles to reduce laser scatter, should greatly improve the quality of data such as these.

Some of our earliest runs were carried out in pure NH_3 , at pressures of 3-4 torr. Dilution in N_2 or Ar, and reduction of the NH_3 partial pressure, improve the signal levels by factors of 30 or more. This may be due to a high quench rate for $\text{NH(A)} - \text{NH}_3$ collisions, or to chemical removal of NH(X) in the presence of NH_3 before reaching the excitation region. The present experiments do not distinguish these possibilities. A separate measurement of the quench rate would be useful, as by measuring the pressure dependence of the lifetime under short pulse excitation (using a N_2 or Nd:YAG laser pumped dye, which is then frequency doubled) or through the response of the fluorescence as the laser power is increased toward optical saturation¹⁸.

IV. SUMMARY

LEF in the A-X system of NH has been demonstrated in a discharge flow of NH_3 . Maps of excitations in the (1,0) and (0,0) bands show a wealth of rotational structure. This promises ready determination of rotational temperatures but demands a relatively narrow-band laser for quantitative measurements of concentrations especially if excitation is in the Q-head region.

The ability to excite both $v'=1$ and $v'=0$ immediately suggests the possibility of state-specific vibrational and rotational energy transfer studies. Scans of the fluorescence in our experiment are of low signal level when we use narrow enough slits to obtain rotationally resolved emission; they do show some relaxation occurring in the presence of N_2 , but not complete thermalization. A better designed flow system than the present one should greatly improve the quality of such data.

From a diagnostic standpoint, it is desirable to pump at one wavelength and observe at a different one, so as to avoid background such as Mie scattering in a particle-laden combustor. The fact that the (0,1) band has transition probability nearly one per cent of that of (0,0) establishes this as a viable method. Alternatively, one could pump in (1,0) and observe the resulting (1,1) and collisionally induced (0,0) emission. This choice of two pump/detection combinations, each in a region covered by a strong laser dye, offers advantages in the event of interfering absorption.

¹⁸J. W. Daily, "Saturation Effects in Laser Induced Fluorescence Spectroscopy", *Appl. Opt.* **16**, 568-571 (1977); A. P. Baronavski and J. R. McDonald, "Measurement of C_2 Concentration in an Oxygen-Acetylene Flame: An Application of Saturation Spectroscopy", *J. Chem. Phys.* **66**, 3300-3301 (1977); J. E. Allen, Jr., W. R. Anderson and D. R. Crosley, "Opto-Acoustic Pulses in a Flame", *Opt. Letters* **1**, 118-120 (1977).

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